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FRANCK-CONDON FACTORS FOR THE B-X SYSTEM OF S_2

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US ARMY ARMAMENT RESEARCH AND DEVELOPMENT COMMAND
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A frequency doubled tunable dye laser has been used to selectively excite individual vibrational levels within v=2 and 6-9 of the B-state of diatomic sulfur. Measurements of the intensity in emission of all the terms returning to ground state vibrational levels permit the determination of absolute Franck-Condon factors. Combined with previous studies, this work completes the set of Franck-Condon factors for bound-bound transitions within the B-X system.

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20. ABSTRACT (Cont'd)

A simple pictorial representation of the Franck-Condon factors is presented and conclusions may be drawn concerning the overlap with the B-state wavefunctions above the predissociation limit.

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I. INTRODUCTION

A simple product form can often be written to express the relationship between the intensity of an emission line in an electronic transition of a diatomic molecule, and the population of the emitting level:

$$I_{v'J'}^{v''J''} = [64\pi^4\nu^4/3c^2][S_{J'J''}/(2J' + 1)]\bar{R}_e^2\, q_{v'v''}N_{v'J'} \quad . \qquad (1)$$

This represents the total energy (erg) emitted each second (into all 4π sterad) from 1 cm^3 of gas containing $N_{v'J'}$ excited state molecules in the level in question. ν is the frequency (Hz) of the transition, which occurs between the upper (single prime) and lower (double prime) vibrational (v) and rotational (J) states. The electronic transition moment $\bar{R}_e$ is here assumed constant for all transitions, an assumption valid[1] for the B-X system of S_2 studied in this work. The contributions due to the nuclear motion, viz., the rotational line strength $S_{J'J''}$ and the vibrational overlap factor (Franck-Condon factor) $q_{v'v''}$, are likewise considered in Eq. (1) to be fully separable. (Small, calculable corrections to the v-dependence of $S_{J'J''}$ and the J-dependence of $q_{v'v''}$ have been discussed.)[1]

There is a variety of experiments in which intensity data are used, together with Eq. (1), to extract populations of individual levels in both ground and excited states. Such applications require reliable values of $S_{J'J''}$ and $q_{v'v''}$ for the electronic system under study. For the $B^3\Sigma_u^-$ - $X^3\Sigma_g^-$ system of S_2, there have been several such investigations recently. These include data on energy transfer within the B-state following selective excitation,[2] and the analysis of chemiluminescence produced in afterglows[3,4] or following the alkaline earth rearrangement

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[1] *K. A. Meyer, "Some Radiative Properties of the $B^3\Sigma_u^-$ State of Diatomic Sulfur", Ph. D. Thesis, University of Wisconsin, 1976; K. A. Meyer and D. R. Crosley, "Intensity Studies on S_2 Selectively Excited by Hg Line Radiation", to be published.*

[2] *T. A. Caughey, "Collisional Energy Transfer in B State Diatomic Sulfur", Ph. D. Thesis, University of Wisconsin, 1977; T. A. Caughey and D. R. Crosley, "Relaxation Within the $B^3\Sigma_u^-$ State of S_2", J. Chem. Phys., 69, 3379 (1978).*

[3] *D. Kley and H. P. Broida, "Chemiluminescence and Photoluminescence of S_2, SO and SO_2 in SF_6 Afterglows", J. Photochem., 6, 241-252 (1976/77).*

[4] *G. Lakshminarayana and C. G. Mahajan, "Spectroscopic Studies of the Sulfur Afterglow", J. Quant. Spectrosc. Radiat. Transfer, 16, 549-552 (1976).*

reaction M + S_2Cl_2.[5] Another application lies in the choice of broad-band filtering for flame photometric analysis of sulfur in the presence of interferences.[6]

As a probe of ground state populations, laser induced fluorescence such as reported here is a most attractive diagnostic tool; at least one other current study[7] has used this technique as a combustion diagnostic for S_2. In addition, photoluminescence from a filtered continuum[3] can also provide ground state data. Finally, these data can be used for further development of the recent optically pumped S_2 laser,[8] which has a broad range of near continuous tunability through the ultra-violet and visible; the widespread occurrence of B-X emission in discharges and chemical reactions offers the possibility of an S_2 chemical laser.

In nearly all cases of diatomic electronic transitions, including the B-X system of S_2, sufficiently accurate values of $S_{J'J''}$ may be obtained by calculation, using measured spectroscopic constants. The Franck-Condon factors can also be theoretically computed to the required accuracy in many cases, using model potentials, most often of RKR form. In the case of the B-X transition, however, such calculations of $q_{v'v''}$ are not reliable, as is illustrated[9] by the disagreement between experimental and calculated values of $q_{3,v''}$ and $q_{4,v''}$ for v'' = 0 through 10. While the calculated Franck-Condon factors exhibit the same qualitative trends as those seen in the measured values, the quantitative disagreement precludes the use of the theoretical quantities for analysis purposes, so that experimental values are necessary.

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[5] *F. Engelke and R. N. Zare, "Crossed-Beam Chemiluminescence: The Alkaline Earth Rearrangement Reaction M + S_2Cl_2 → S_2^* + MCl_2", Chem. Phys., 19, 327-340 (1977).*

[6] *S. S. Brody and J. E. Chaney, "The Application of a Specific Detector for Phosphorous and for Sulfur Compounds - Sensitive to Nanogram Quantities", J. Gas Chromatog., 4, 42-46 (1966); P. J. Maroulis and A. R. Bandy, "Estimate of the Contribution of Biologically Produced Dimethyl Sulfur to the Global Sulfur Cycle", Science, 196, 647 (1977).*

[7] *C. H. Moeller, II, K. Schofield, M. Steinberg, and H. P. Broida, "Sulfur Chemistry in Flames", Seventeenth Symposium (International) on Combustion, Leeds, England, August 1978.*

[8] *S. R. Leone and K. G. Kosnik, "A Tunable Visible Ultraviolet Laser on S_2 ($B^3\Sigma_u^-$ - $X^3\Sigma_g^-$)", Appl. Phys. Lett., 30, 346-348 (1977).*

[9] *K. A. Meyer and D. R. Crosley, "Franck-Condon Factors From Selectively Excited Resonance Fluorescence in the B-X System of S_2", J. Chem. Phys., 59, 3153-3161 (1973).*

Although the B-X system in discharge emission is too heavily congested to permit reliable intensity measurements over but a small range of bands, it is an ideal candidate for study using the technique of selective excitation of resonance fluorescence. The method is schematically illustrated in Figure 1. A laser is tuned to some specific absorption line of the (9,1) band, exciting the S_2 to a particular triplet component of a particular rotational level in v' = 9 (the rotational and triplet structure is not explicitly shown in Figure 1). From here the S_2 radiates to all of the v'' levels for which the $q_{v'v''}$ are non-negligible; several of these are indicated in the figure. The experiment consists of the measurement of the relative intensities of these transitions; because all the fluorescent terms are monitored, absolute values of $q_{v'v''}$ may be extracted from the data.

Earlier work by Meyer[1,9] utilized atomic line selective excitation of individual v'J' levels of the $B^3\Sigma_u^-$ state, furnishing the Franck-Condon factors for v' = 0, 1, 3, 4, and 5. In the current study, a frequency doubled, tunable dye laser has served as the excitation source, enabling measurements to be made on v' = 2 and 6 through 9. The combination of these results forms the full set of $q_{v'v''}$ for all the bound-bound vibrational bands of the B-X system of the 32-32 isotope.

II. EXPERIMENTAL DETAILS

The apparatus used in the experiment is illustrated schematically in Figure 2. The sulfur is maintained in an evacuable all-quartz cell; the pressure is held at ∿100 mtorr by a sidearm reservoir at ∿110°C, and the body cell is kept at ∿600°C to ensure a high concentration ($\geq$ 98%) of the S_2 species. The exciting photons are provided by a flashlamp pumped dye laser which is frequency doubled (Chromatix CMX4), and into which an intracavity etalon may be inserted.

Several parameters are monitored during an experiment in order to prevent errors caused by drift in either the laser intensity or frequency. The essential results of the experiment are provided by a scanning 0.35m monochromator (#I), outfitted with an EMI 9558Q photomultiplier (PMT) and usually operated with 75μ slits. After preamplification, and subsequent attenuation if necessary, the PMT output is fed to channel A of a dual-input boxcar integrator. A second monochromator, #II, having an EMI 6255 PMT detector, is operated with wide slits (2 mm) and at a fixed wavelength. This wavelength corresponds to that of one of the more intense terms of the fluorescent series emitted by the particular v' excited by the laser. After preamplification, this forms the input to channel B. In addition, a small portion of the ultraviolet light is split off prior to entering the sulfur cell, and detected by a third PMT whose average current is measured. The input to channels A or B, and the corresponding boxcar gages, are observed on an oscilloscope. Recorder traces are made of the boxcar output of channel A ÷ channel B v. the wavelength of monochromator I, and the integral of this quantity over wavelength for each

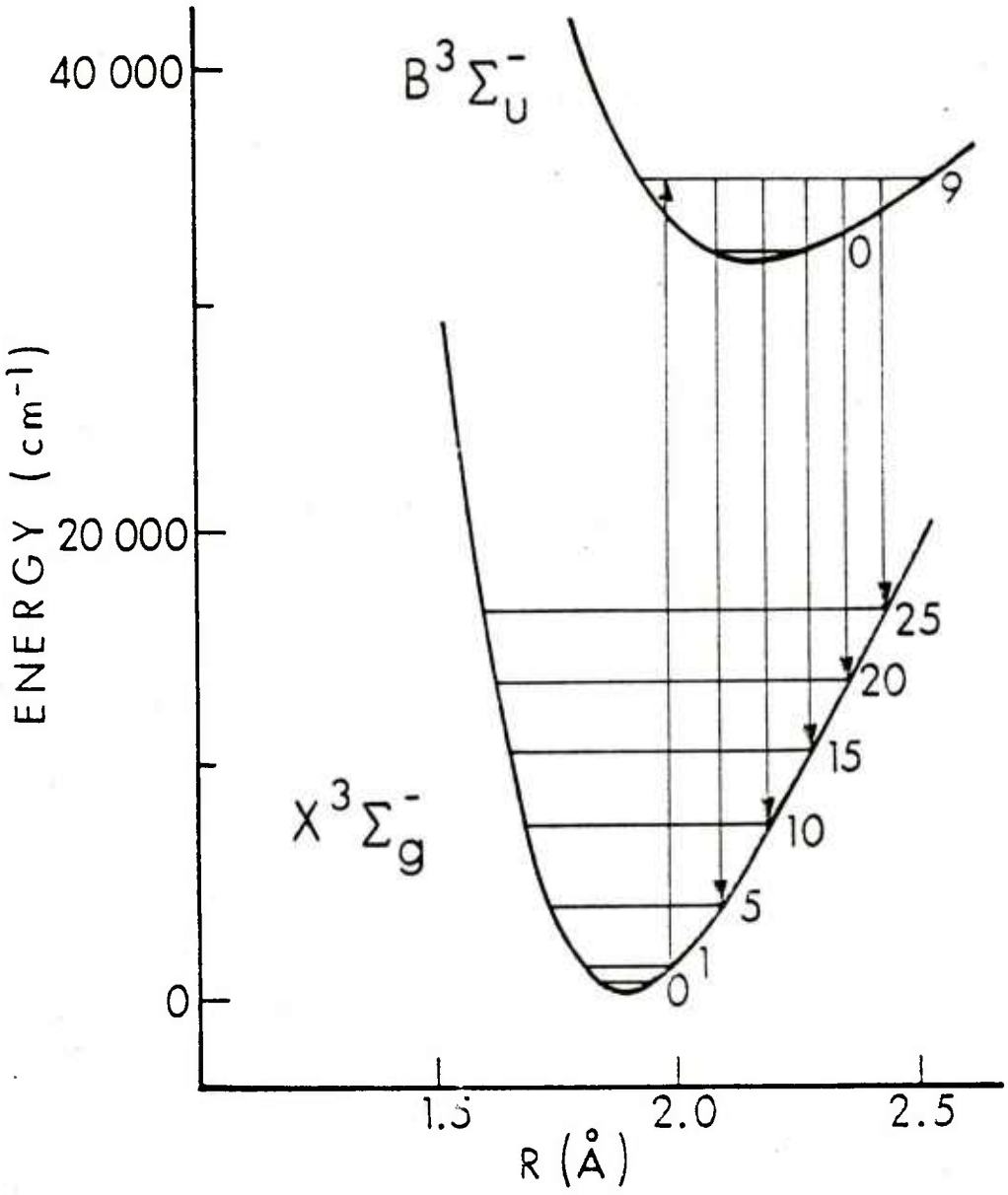

Figure 1. Schematic illustration of the experiment. The laser is tuned to a specific rotational line (rotational levels are not shown on the diagram) of the (9,1) band, exciting v' = 9. Emission is observed to many v'' levels, a few of which are indicated.

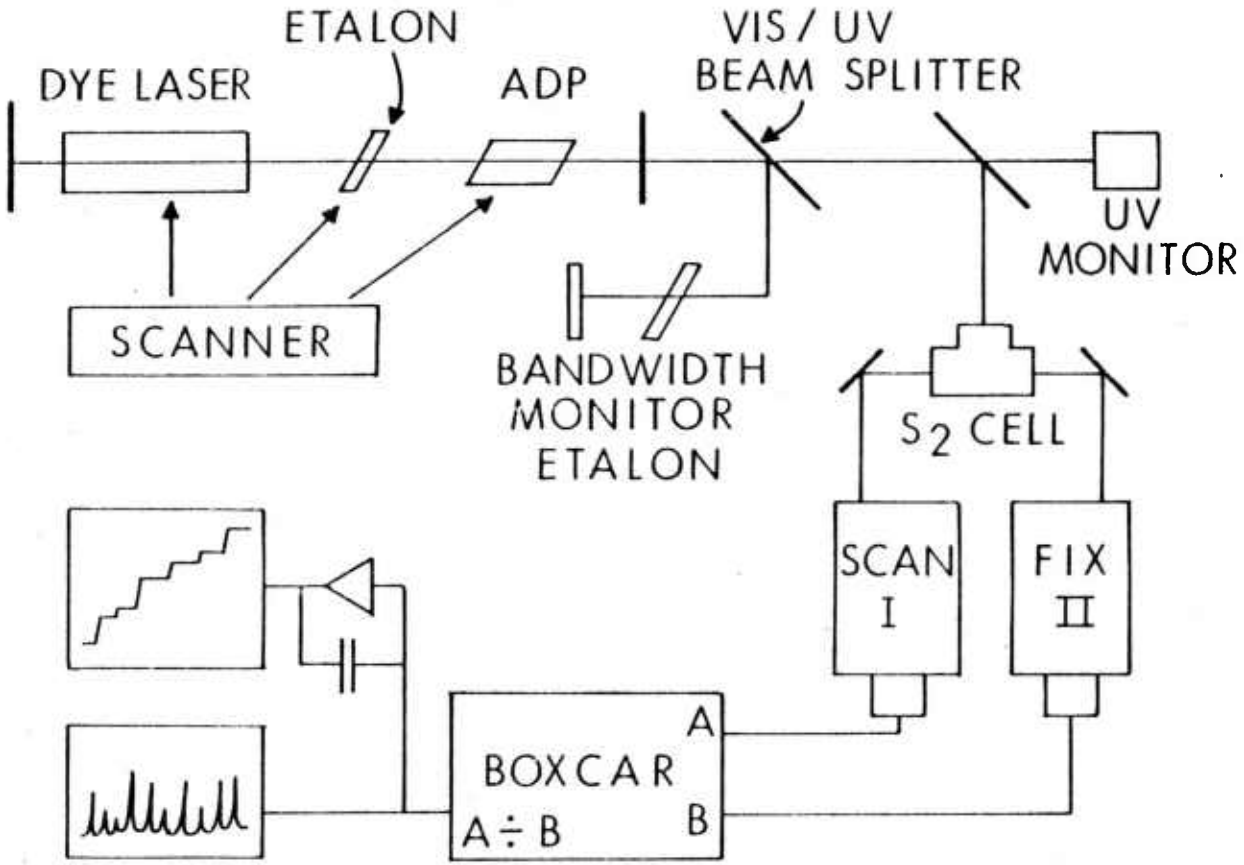

Figure 2. Experimental arrangement. The narrow-band, tunable, frequency doubled dye laser irradiates the S_2, whose fluorescence is measured by a scanning monochromator (I) and monitored by another (II) at fixed wavelength. A boxcar integrator, triggered by the laser pulse, yields the ratio of the two outputs, which is integrated as well as recorded directly.

band which forms the raw experimental data). Also, we monitor, and sometimes record, the output of channel B, providing a measure of the laser amplitude and frequency drift, and the ultraviolet-detecting PMT, which yields a measure of the laser power. In addition, the small amount of visible light emitted by the laser passes through a small etalon; the resulting fringe pattern on a screen is checked visually to ensure that the proper line narrowing by the intracavity etalon is maintained.

A 20 cm long fiber optic rod collects light from the flashlamp and delivers it to an enclosed photodiode mounted above a fast amplifier. The photodiode output forms the trigger pulse for the boxcar and scope. An earlier mode of triggering using a synchronization pulse keyed to the laser spark gap circuitry proved unreliable due to jitter in the flashlamp firing time, whereas the photodiode trigger was quite stable.

The bandwidth of the laser, in the etalon-narrowed configuration used for the runs, is $\sim$0.3 cm^{-1} in the ultraviolet. Individual rotational absorption lines were often congested even on this scale, and some effort was necessary in order to find a line in each absorption band which was free of overlap. The laser was first scanned in the unnarrowed mode ($\sim$10 cm^{-1} bandwidth) and the fluorescence monitored, as a function of laser wavelength, by monochromator, II. This produces an excitation spectrum such as that shown in Figure 3 for a scan of the (6,0) band. Narrowing the laser line and scanning a smaller region produces the more highly resolved excitation spectrum also shown in Figure 3, though this is still not fully free from overlapped excitation lines. After choosing a suitable candidate for excitation, the rotationally resolved fluorescence spectrum for a given term or terms is scanned with monochromator I. This produces a characteristic two or three-line pattern whose spectral purity is further ascertained by slight detuning of the laser, and rescanning to check for overlap.

In Figure 4 is shown an exemplary recorder tracing of the fluorescence progression obtained by scanning monochromator I while exciting the $N' = 36$, $J' = 37$ level of $v' = 6$. Each term consists of the apparent three-line pattern shown expanded for $v'' = 1$. The seven-lobe undulatory pattern in the scan admits of a simple interpretation discussed more fully below.

The response of the monochromator-PMT combination as a function of wavelength was measured using a GE DXW tungsten halide lamp with an NBS-traceable calibration curve.

It is necessary to ascertain that reabsorption of the emission by ground state S_2, between the emitting region and the cell exit window, does not affect the measured results for the low v'' terms. Intensities were measured for at least three reservoir temperatures encompassing that used for the actual runs, and an extrapolation was made to zero pressure. See Appendix I for further details.

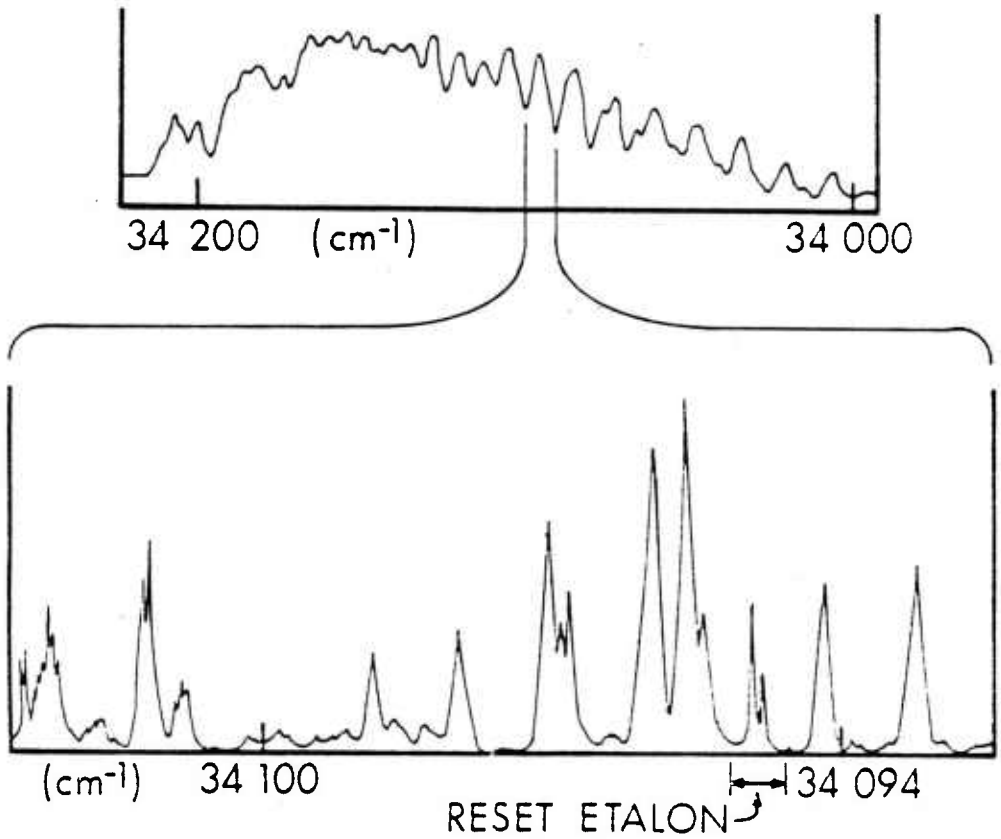

Figure 3. Excitation scans of the (6,0) band. The laser wavelength is scanned while the output from monochromator II is measured. (Top) Laser bandwidth 12 cm^{-1} (Bottom). A small region of the scan shown on top, with the laser bandwidth here 0.3 cm^{-1}.

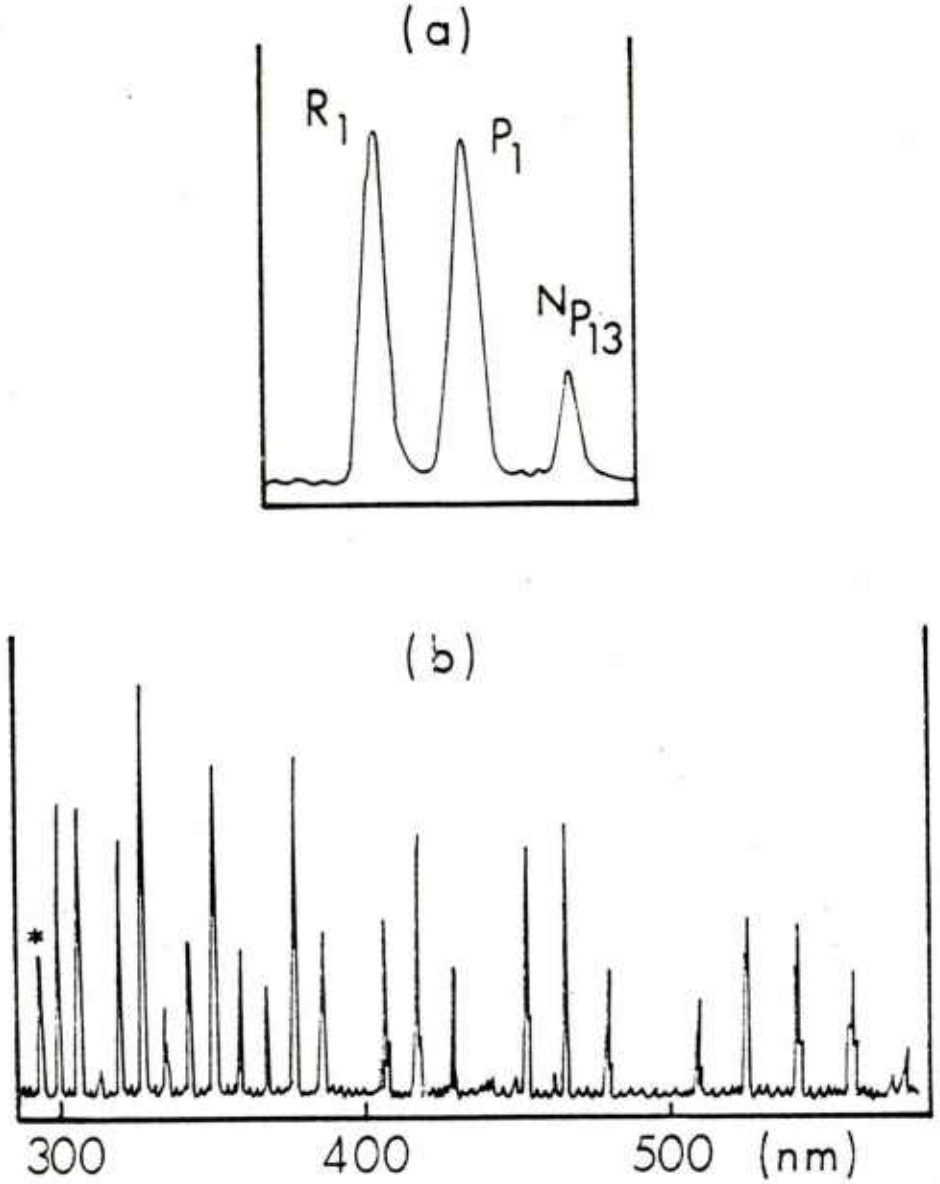

Figure 4. Scans of the fluorescence obtained exciting the v' = 6, N' = 36, J' = 37 level of $B^3\Sigma_u^-$. (a) Scan of the rotational structure in the (6,1) term. The R_1 - P_1 splitting is 3.85A. A $^PR_{13}$ branch is also present but overlapped by the P_1 line. (b) Scan of the entire fluorescence progression emitted by v' = 6. The asterisk marks the exciting band, (6,0). Terms are visible here out to v'' = 26. Each term consists of the same rotational structure shown in (a).

III. DATA ANALYSIS AND RESULTS

The measured intensity for a particular v" term, $F_{v'v''}$ is obtained from the recorder trace representing the integral, over the full wavelength range of that term, of the A B boxcar input. While this normalization provides adequate correction for small drifts in laser power, the doubling crystals must occasionally be peaked up during the scan of a single progression. When such drift is present, a term of low v" having high measured intensity is rescanned to provide correct ratios.

For the fluorescent term corresponding to the excitation band, there is some laser scatter present at the wavelength of the exciting rotational branch. The intensity for this particular term is then obtained from the ratio of the peak heights of the non-overlapped rotational branch in that term, and the corresponding rotational branch of a neighboring intense term.*

These measured intensities are corrected for the detector response $R(\nu)$ and divided by the ν^4 factor.** This yields a series of measured quantities strictly proportional to $\Sigma_{J''} \overline{R_e^2}\, S_{J'J''}\, q_{v'v''}$. We assume that the electronic transition moment is independent of internuclear distance, so that $\overline{R_e^2}$ is the same for all (v', J', v", J"). This constancy is borne out by the lack of any discernible overall smooth trends in the $q_{v'v''}$ measured here or previously;[1,9] a more complete discussion of this point may be found elsewhere.[1] Since we integrate over all the rotational branches of the fluorescent emission, and since $\Sigma_{J''} S_{J'J''} = 2J' + 1$, no corrections for the vibrational dependence[10] of $S_{J'J''}$ need be made. Thus, the $F_{v'v''}/\nu^4 R(\nu)$ form a set of values, each proportional to the Franck-Condon factor $q_{v'v''}$ for that term.

Now the sum, over all v", of the $q_{v'v''}$ for a particular v', is unity:

$$\sum_{v''} q_{v'v''} = 1 \quad . \tag{2}$$

This also alleviates concerns about contributions due to stimulated emission, which is present in the rotational branch overlapped by the laser, at the spectral power densities used.

**The PMT actually measure photons sec^{-1}, not erg sec^{-1}, but the calibration using the standard lamp is done so as to obtain an effective response in the latter units.*

[10] *Such a correlation should be applied to the intensities of the rotationally resolved branches used to determine the intensity of the excitation term; however, this is a negligible amount. See K. A. Meyer and D. R. Crosley, "Rotational Satellite Intensities and Triplet Splitting in the $B^3\Sigma_u^-$ State of S2", Can. J. Phys., 51, 2119-2124 (1973).*

The rationale for this relationship is perhaps most readily evident by an expansion of the upper state vibrational wavefunction $\psi_{v'}$ in terms of the complete set of ground state vibration wavefunctions $\psi_{v''}$:

$$\psi_{v'} = \Sigma_{v''} a_{v'v''}\psi_{v''} \quad .$$

But

$$|a_{v'v''}|^2 = |\int \psi_{v'}(r)\psi_{v''}(r)dr|^2 \equiv q_{v'v''} \qquad (3)$$

(where r is the internuclear distance), and the orthonormality of the $a_{v'v''}$ directly yields Eq. (2). It is necessary in this context to note that the continuum vibrational wavefunctions of the X-state lie above the bound vibrational wavefunctions of the B-state, so that the sum is effectively over the bound wavefunctions only.

Consequently, by Eq. (2), the normalization of our measured intensities to unit sum directly yields the absolute Franck-Condon factor for each term. This is possible since the cleanliness of the emission afforded by the selective excitation process permits us to measure <u>all</u> of the terms in the fluorescence progression. The values obtained are collected in Tables 1 through 5.

The uncertainty in the individual measured intensity of each term, $\delta F_{v'v''}$, has been estimated from the chart recorder output. The resulting error bars in the $q_{v'v''}$ are of two kinds, both of which are listed in Tables 1 through 5. The first, designated $\delta q_{v'v''}$, is directly proportional to the measured uncertainty $\delta q_{v'v''} = q_{v'v''}\ \delta F_{v'v''}/F_{v'v''}$. This is the pertinent uncertainty to be used when comparing the <u>ratio</u> of any of the measured Franck-Condon factors, e.g., in a determination of the temperature or a measurement of product distributions in chemiluminescence.

The uncertainties $\delta q_{v'v''}$ also lead to a total uncertainty in the sum used for the normalization. Consequently, the uncertainty in the <u>absolute</u> value of each $q_{v'v''}$ contains a contribution from this source as well as from the $\delta q_{v'v''}$. These uncertainties in the absolute Franck-Condon factors, termed $\Delta q_{v'v''}$, are those necessary for such purposes as absolute absorption strength calculations, and laser design considerations. The $\Delta q_{v'v''}$ are calculated as the square root of the sum of the squares of $\delta q_{v'v''}$ and the normalization uncertainty.

It should be stressed that our values of $q_{v'v''}$ are of course only as accurate as the calibration of the spectrometer and PMT using the standard lamp. Since we require only the relative output of the lamp as a function of wavelength, an uncertainty of the order of only 1-2%

TABLE I. FRANCK-CONDON FACTORS AND UNCERTAINTIES FOR v' = 2 EXCITED LEVEL IS F_3 (46)

v''	$10^3 q$	$10^3 \delta q$	$10^3 \Delta q$
0	1.3	0.2	0.2
1	11.7	0.4	0.7
2	40.3	3.8	4.4
3	112.7	2.9	6.7
4	116.1	5.0	8.0
5	77.0	2.0	4.6
6	20.0	1.2	1.6
7	4.5	0.5	0.6
8	40.5	1.8	2.8
9	72.6	3.1	5.0
10	60.3	1.8	3.7
11	16.3	1.5	1.7
12	1.6	0.6	0.6
13	21.5	1.5	1.9
14	65.2	3.7	5.1
15	72.3	3.4	5.2
16	101.6	3.3	6.4
17	76.4	2.6	4.9
18	45.6	2.1	3.2
19	21.5	1.9	2.2
20	14.5	1.4	1.6
21	6.5	2.6	2.6
22	<2.0	2.0	---

TABLE 2. FRANCK-CONDON FACTORS AND UNCERTAINTIES FOR v' = 6 EXCITED LEVEL IS $F_1(34)$

v''	$10^3 q$	$10^3 \delta q$	$10^3 \Delta q$
0	26.6	5.4	6.2
1	76.6	2.4	8.8
2	53.5	2.2	6.3
3	3.4	0.8	0.9
4	32.1	3.2	4.8
5	58.3	4.1	7.7
6	5.5	1.8	1.9
7	21.2	2.5	3.4
8	50.8	2.1	6.0
9	13.1	1.3	2.0
10	7.3	1.8	2.0
11	48.8	2.0	5.8
12	27.1	1.0	3.2
13	2.0	1.0	1.0
14	29.0	1.1	3.4
15	47.1	1.6	5.5
16	13.0	1.8	2.3
17	<1.8	1.8	---
18	66.8	4.1	8.5
19	77.5	5.3	10.1
20	21.3	8.9	9.2
21	9.7	4.9	5.0
22	29.4	4.7	5.7
23	75.5	7.7	11.4
24	69.2	4.6	9.0
25	69.9	12.5	14.7
26	37.7	9.4	10.3
27	27.4	13.7	14.0
28	<10.0	10.0	---

TABLE 3. FRANCK-CONDON FACTORS AND UNCERTAINTIES FOR v' = 7 EXCITED LEVEL IS F_3 (30)

v''	$10^3 q$	$10^3 \delta q$	$10^3 \Delta q$
0	46.5	1.4	5.4
1	79.6	7.7	11.7
2	40.6	1.8	4.9
3	8.2	2.1	2.3
4	62.9	4.5	8.3
5	24.9	4.2	5.0
6	9.0	2.8	3.0
7	15.0	0.6	1.8
8	20.5	2.5	3.4
9	7.8	2.6	2.7
10	44.3	2.7	5.6
11	22.3	1.1	2.7
12	<1.9	1.9	---
13	38.1	2.5	4.9
14	28.6	2.9	4.3
15	<2.0	2.0	---
16	28.7	3.0	4.4
17	38.8	3.3	5.4
18	22.0	2.8	3.7
19	<1.9	1.9	---
20	50.2	5.0	7.5
21	68.6	4.9	9.1
22	27.1	5.4	6.2
23	<2.0	2.0	---
24	19.8	5.0	5.5
25	16.6	9.2	11.5
26	86.0	7.7	12.3
27	64.2	6.4	9.6
28	54.6	9.1	10.9
29	30.1	10.0	10.5
30	<2.0	2.0	---

TABLE 4. FRANCK-CONDON FACTORS AND UNCERTAINTIES FOR v' = 8 EXCITED LEVEL IS N' = 28

v''	$10^3 q$	$10^3 \delta q$	$10^3 \Delta q$
0	43.0	4.6	5.7
1	71.9	2.9	6.3
2	4.4	0.6	0.7
3	37.9	3.0	4.2
4	50.7	3.2	5.1
5	<0.6	0.6	---
6	43.5	3.1	4.6
7	38.0	3.1	4.3
8	0.9	0.4	0.4
9	44.1	2.5	4.2
10	24.7	1.3	2.3
11	3.2	0.1	0.3
12	45.8	2.3	4.2
13	23.7	1.4	2.3
14	1.8	0.1	0.2
15	39.1	1.8	3.5
16	28.2	1.0	2.4
17	<0.2	0.2	---
18	29.0	1.3	2.6
19	46.7	1.7	4.0
20	8.6	0.4	0.8
21	6.3	0.6	0.8
22	42.4	2.1	3.9
23	45.6	2.4	5.0
24	12.5	1.2	1.5
25	2.3	1.2	1.2
26	31.7	1.0	2.7
27	65.9	3.0	5.9
28	76.9	7.6	9.7
29	74.1	4.9	7.6
30	36.8	8.6	9.1
31	20.0	10.0	10.1
32	<2.0	2.0	---

TABLE 5. FRANCK-CONDON FACTORS AND UNCERTAINTIES FOR v' = 9 EXCITED LEVEL IS F_1 (36)

v''	$10^3 q$	$10^3 \delta q$	$10^3 \Delta q$
0	82.5	11.7	14.6
1	70.2	3.5	8.2
2	0.6	0.2	0.2
3	57.8	2.9	6.7
4	23.0	1.1	2.7
5	14.7	0.8	1.7
6	53.4	2.7	6.2
7	2.0	0.4	0.5
8	35.1	1.8	4.1
9	40.0	2.0	4.7
10	0.3	0.1	0.1
11	39.1	2.0	4.6
12	22.9	1.2	2.7
13	3.8	0.2	0.4
14	43.2	2.1	5.0
15	18.5	1.2	2.3
16	3.9	0.2	0.5
17	38.3	1.9	4.4
18	25.9	1.8	3.3
19	0.6	0.4	0.4
20	31.9	3.7	5.0
21	39.9	2.0	4.6
22	5.1	0.7	0.9
23	11.2	1.2	1.7
24	41.6	3.3	5.5
25	35.9	2.4	4.5
26	6.2	1.9	2.0
27	2.0	1.0	1.0
28	31.6	5.5	6.4
29	64.7	5.5	8.7
30	91.2	10.0	13.8
31	50.5	6.1	8.1
32	12.2	6.1	6.2
33	<6.0	6.0	---

in the absolute $q_{v'v''}$ is estimated[1] as arising from the calibration. This is not included in the numerical values for $\Delta q_{v'v''}$ given in the tables.

For each excitation, the values of J' for the level excited are determined by a measurement of the splitting[11] between the main R-P doublet (See Figure 4a) for several intense terms in the progression. Appendix II contains details concerning the analysis; the result for each excitation is listed in the tables of $q_{v'v''}$. The Franck-Condon factors in S_2 are observed[1] to vary somewhat with J'. However, the amount of the variation[1] is such that the reported values of $q_{v'v''}$, measured here for J' in the vicinity of 30, are quantitatively correct* for J' between 1 and approximately 50. This includes the important band head region, and the J' corresponding to the peak of the rotational distribution for temperatures of 2000° or less.

IV. DISCUSSION

A. Absolute $q_{v'v''}$ for the B-X System

Together with the measurements made by Meyer,[1,9] these results complete the set of Franck-Condon factors for the B-X system of $^{32}S_2$. All of the values are collected in Table 6, where the entries are given (for convenience) in the form $1000q_{v'v''}$.

B. A Graphical Representation of the $q_{v'v''}$

A simple undulatory pattern, like that exhibited in Figure 4b for the fluorescence progression emitted by v' = 6, is observed for each v'. In particular, the locus of the peaks of the intensities forms a pattern always having (v' + 1) lobes. This result is amenable to a simple explanation[9] and a graphical representation which are described in the following.

Referring to Figure 1, it can be seen that the B-state vibrational wavefunctions have significant amplitude only over a range of internuclear distance where the ground state potential is attractive. This means that the primary contribution of $\psi_{v''}$ to $q_{v'v''}$ will come from the region nearer the right hand turning point, $r_R(v'')$, for that v''.

In the left hand part of Figure 5, the v' = 9 and several v'' wavefunctions are drawn. Consider the overlap of v' = 9 with v'' = 20. The more rapid oscillations in the center of the v'' = 20 wavefunction will

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[11] *K. A. Meyer and D. R. Crosley, "Hanle Effect Lifetime Measurements on Selectively Excited Diatomic Sulfur", J. Chem. Phys., 59, 1933-1941 (1973).*

* *I. e. within the quoted error bars.*

TABLE 6. FRANCK-CONDON FACTORS FOR THE B-X SYSTEM. ENTRIES ARE 1000 x $q_{v'v''}$, EXCEPT FOR THE LAST COLUMN, WHICH IS THE FRACTIONAL OVERLAP WITH THE CONTINUUM FOR THE v'' LEVEL

v'' \ v'	0	1	2	3	4	5	6	7	8	9	f
0	<1	1	1	4	9	15	27	47	43	83	0.77
1	1	6	12	21	39	48	77	80	72	70	0.57
2	10	25	40	67	82	80	54	41	4	1	0.60
3	23	55	113	100	69	39	3	8	38	58	0.49
4	41	103	116	72	11	14	32	63	51	23	0.47
5	64	112	77	6	11	43	58	25	<1	15	0.59
6	105	98	20	17	61	57	6	9	44	53	0.53
7	136	70	5	67	54	9	21	15	38	2	0.58
8	152	<3	41	69	5	18	51	21	1	35	0.61
9	143	23	73	20	16	56	13	8	44	40	0.56
10	118	45	60	3	62	29	7	44	25	<1	0.61
11	82	82	16	48	46	<3	49	22	3	39	0.61
12	58	100	2	76	3	28	27	<2	46	23	0.64
13	38	93	22	54	15	6	2	38	24	4	0.70
14	16	80	65	6	56	20	29	29	2	43	0.65
15	7	65	72	7	54	<4	47	<2	39	19	0.69
16	2	29	102	38	21	31	13	29	28	4	0.70
17	<1	20	76	72	1	50	<2	39	<1	38	0.70
18		<10	46	87	27	41	67	22	29	26	0.66
19			22	72	74	11	78	<2	47	1	0.70
20			15	47	87	15	21	50	9	32	0.72
21			7	32	77	61	10	69	6	40	0.70
22			<2	11	62	76	29	27	42	5	0.75
23				3	34	66	76	<2	46	11	0.76
24				<2	17	60	69	20	13	42	0.78
25					7	42	70	17	2	36	0.83
26					<1	15	38	86	32	6	0.82
27						13	27	64	66	2	0.83
28						<16	<10	55	77	32	0.84
29								30	74	65	0.83
30								<2	37	91	0.87
31									20	51	0.93
32									<2	12	0.99
33										<6	----
Ref.	1	1	--	9	9	1	--	--	--	--	

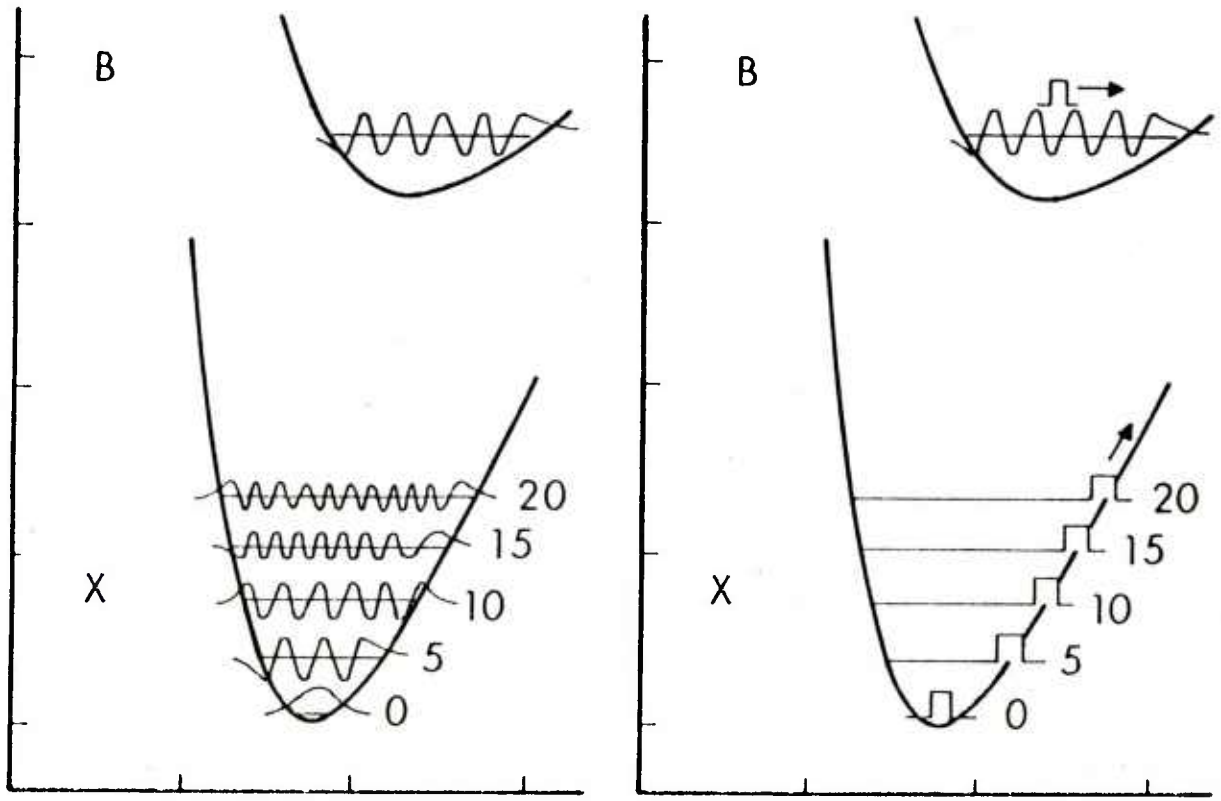

Figure 5. (Left) Potential curves and several wavefunctions for the B and X states of S_2. (Right) Schematic replacement of the ground state wavefunctions by a gate attached at the right hand turning point. Increasing v" in effect scans the gate to larger internuclear distance, tracing out $|\psi_{v'}|^2$ (see text).

yield alternating positive and negative values when multiplied by the more slowly varying $\psi_{v'}$ at the same value of r (See Eq. (3)). Consequently, the contributions to the overlap integral from the middle region of internuclear distance will tend to cancel, and the integral will be dominated by contributions from the region near $r_R(v'')$ where $\psi_{v''} = 20$ has a more slowly varying amplitude.

This argument is extended graphically in the right hand portion of Figure 5, where the more rapidly oscillating part of the $\psi_{v''}$ (which give zero or small net overlap) is set to zero, and the lobe near $r_R(v'')$ replaced by a gate attached at the turning point. As the spectrometer scans the fluorescent progression, as in Figure 4b, the gate moves to higher v'' and hence, larger $r_R(v'')$ in effect scanning across $\psi_{v'}$ (See Figure 5). Considering the gate to be represented mathematically as a delta function, we have

$$q_{v'v''} = \left| \int \psi_{v'}(r)\delta(r-r_R(v''))dr \right|^2 = \left| \psi_{v'}(r_R(v'')) \right|^2 . \qquad (4)$$

That is, the Franck-Condon factor $q_{v'v''}$ represents the square of the probability amplitude for the v' vibrational level at the value of internuclear distance given by $r_R(v'')$.

[Clearly, Eq. (4) represents an approximation needed for the purposes of discussion, rather than a quantitative relationship. However, model calculations for v' = 4 using Morse wavefunctions[12] have been carried out. These show that, while one must integrate inward from $r_R(v'')$ for 3 or 4 oscillations of $\psi_{v''}$ before the cancellation becomes appreciable, qualitatively correct calculated values of $q_{4,v''}$ are obtained by terminating the integral after the first lobe at $r_R(v'')$.]

This simple picture can be graphically represented in the following fashion. The right hand turning points $r_R(v'')$ are obtained from RKR calculations[13] on the ground state. The $q_{v'v''}$ from Table 6 are then plotted, in stick diagram fashion, as a function of $r_R(v'')$. For each v', the $q_{v'v''}$ are plotted with zero at the corresponding energy level (that is, in the way that wavefunctions are often plotted).

The results are displayed in Figure 6. Superimposed on the $q_{v'v''}$ pattern is the RKR curve for the B-state.[13] It is to be emphasized

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[12] *G. D. Brabson, "Calculation of Morse Wave Function with Programmable Desktop Calculators", J. Chem. Ed., 50, 397-399 (1973).*

[13] *G. D. Brabson and R. L. Volkmar, "Calculation of Potential Energy Curves for S_2 Perturbed by a Frozen Inert Gas Matrix Environment", J. Chem. Phys., 58, 3209-3215 (1973).*

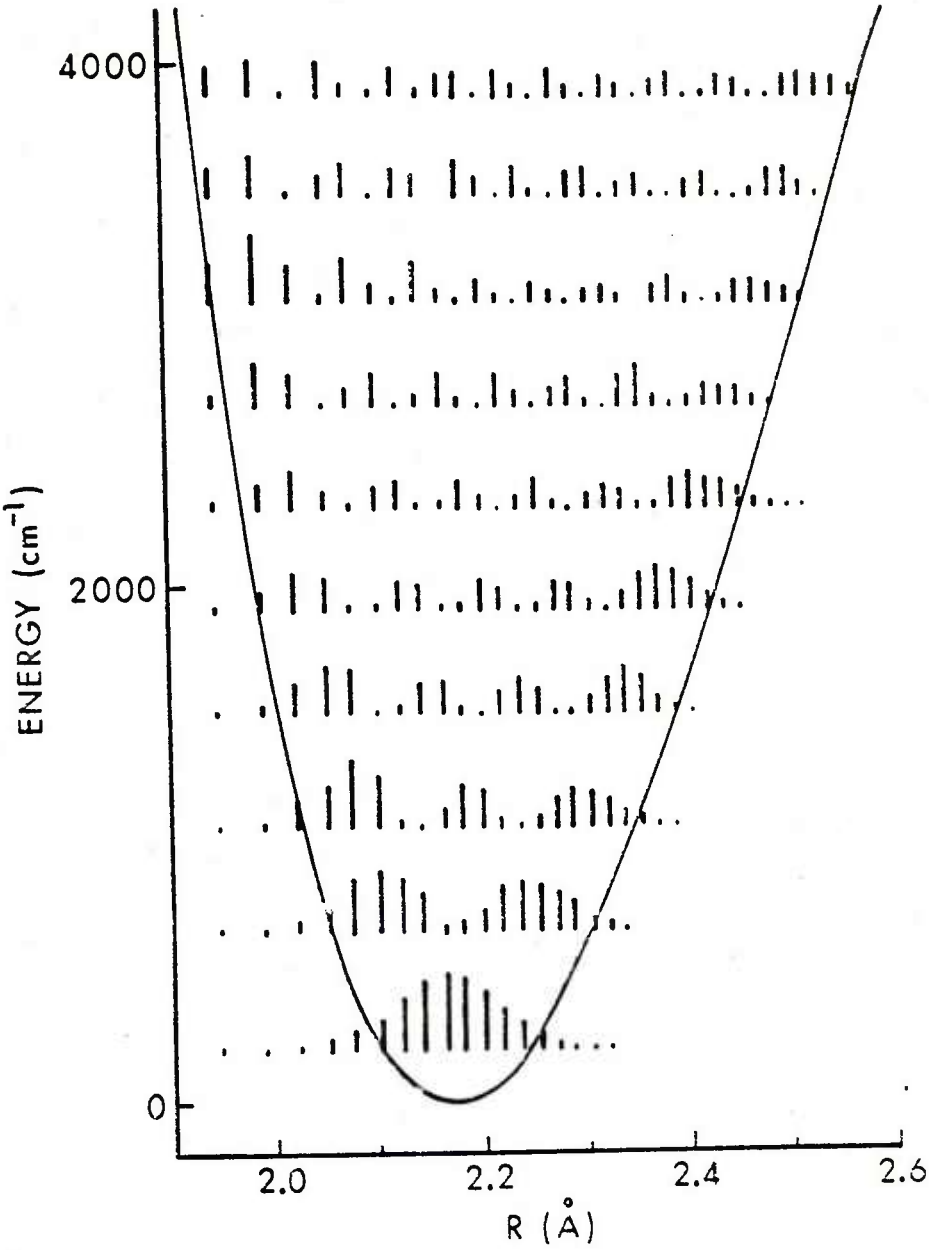

Figure 6. A plot of the $q_{v'v''}$ vs. $r_R(v'')$; see text. The zero for each $q_{v'v''}$ is placed at the corresponding energy level for that v'. The curve is the B-state RKR potential, independently plotted.

that the potential curve plot and the $q_{v'v''}$ plots shown in Figure 6 are entirely independent* of one another.

The assumptions involved in the use of Eq. (4) preclude attaching quantitative significance to Figure 6. Nonetheless, we find the representation exhibited there to be pleasing and instructive. The "wavefunctions" possess the proper number of lobes and span the expected range of internuclear distance with reasonable centering. It is tempting to point out, additionally, that the undulations in the center (where the kinetic energy is higher) have a shorter wavelength than those near the turning points, and that the plots show finite though small amplitude in the classically forbidden region outside the turning points. In any event, these results form a compelling reminder that molecular vibration is indeed described by a wavelike picture;[14] in fact, the essence of this illustration is contained clearly in the raw data, such as that displayed in Figure 4b.

C. Overlap with $\psi_{v'}$ above the Predissociation Limit

The Franck-Condon factors, for a given $\psi_{v''}$, obey a sum rule like Eq. (2) when summed over v'. However, in this case the sum must also include those vibrational levels above the predissociation limit in $B^3\Sigma_u^-$, which sets in just below the rotationless level in v' = 10 (for the 32-32 isotope). One may write

$$\sum_{v'=0}^{9} q_{v'v''} + f_{v''} = 1 \qquad (5)$$

where $f_{v''}$ represents the fraction of the total overlap of $\psi_{v''}$ with those v' wavefunctions above this limit. The $f_{v''}$ may be easily evaluated by summing over the $q_{v'v''}$; the results are listed in Table 6.

A clear trend may be discerned in the $f_{v''}$. (A quantitative attempt at uncertainty assessment is unwarranted; small differences between any two $f_{v''}$ are likely not significant but the overall variation should be meaningful.) With the exception of v'' = 0, the overlap with the $\psi_{v'}$ above v' = 9 rises rather smoothly from a value near 50% for low v'' to a value above 90% for v'' in the vicinity of 30.

The zero of energy must of course be defined.

[14] *To quote the late E. U. Condon ["The Franck-Condon Principle and Related Topics", Amer. J. Phys., 15, 365-374 (1947)]: "The Franck-Condon patterns form real and forceful proof ... of the reality of de Broglie waves associated with the nuclear motions in the molecules". We thank Dr. R. N. Zare for drawing our attention to this delightful and instructive article.*

The value of $f_{v''}$ for v'' = 0 is obviously outside the general trend. It is important to establish that this is a real difference, and not some systematic experimental error or artifact of the calculation procedure. To do so, we offer the following qualitative physical argument based on the same kind of approach used to arrive at the plot in Figure 6.

Again referring to Figure 1, we this time note that the $\psi_{v''}$, for low values of v'', span a region of internuclear distance situated under the left-hand (repulsive) portion of the B-state potential. The same line of reasoning as before can now be used to consider that, for a given v'', the set of $q_{v'v''}$ represents the values $|\psi_{v''}(r_L(v'))|^2$, the square of the probability amplitude at the left-hand turning point of the B-state potential. In this case, however, examination of Figure 1 suggests that the approximation should break down by the time $v'' \sim 10$.

In Figure 7 is presented a plot akin to that in Figure 6, for $0 < v'' < 10$. Brabson's calculations[13] furnish the $r_L(v')$, as well as the X-state potential curve which is again independently* superimposed. The abrupt termination of the plots at $r_L(v' = 9) = 1.928\text{Å}$ is of course due to the fact that the left-hand turning points less than this value belong to vibrational levels above the predissociation limit.

For the lowest values of v'', one can discern the essential outlines of the right-hand portion of the "wavefunctions" showing reasonably spaced lobes of the proper number. On the other hand, the pattern becomes lost at the higher values of v'' plotted in Figure 7, as anticipated from the examination of the potentials.

Considering only a comparison of $\psi_{v''=0}$ with the v'' = 1 through 3 patterns, it can be seen that the former has a larger fraction of its amplitude in the region where $r < r_L$ (v' = 9). Consequently, it may be expected to have a significantly larger overlap with the predissociated levels v' > 10. Even though those v' levels are not bound, they too will have more slowly varying lobes near their (single) turning point at the repulsive wall. The v'' = 0 wavefunction exists in a region probably corresponding to that spanned by the rapidly rising B-state potential, yielding good overlap with these wavefunctions.

Herzberg and Mundie[15] have taken absorption spectra of the (v', 0) sequence up to v' = 22. The intensity in absorption jumps abruptly between v' = 9 and 10, corresponding to the onset of the predissociation. The relative intensities from v' = 10 through v' = 22 form a smooth pattern with a single maximum at v' = 13, strongly suggestive of the continuation, to the left, of the pattern for v'' = 0 in Figure 7. Their

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The zero of energy must of course be defined.

[15] *G. Herzberg and L. G. Mundie, "On the Predissociation of Several Diatomic Molecules", J. Chem. Phys., 8, 263-273 (1940).*

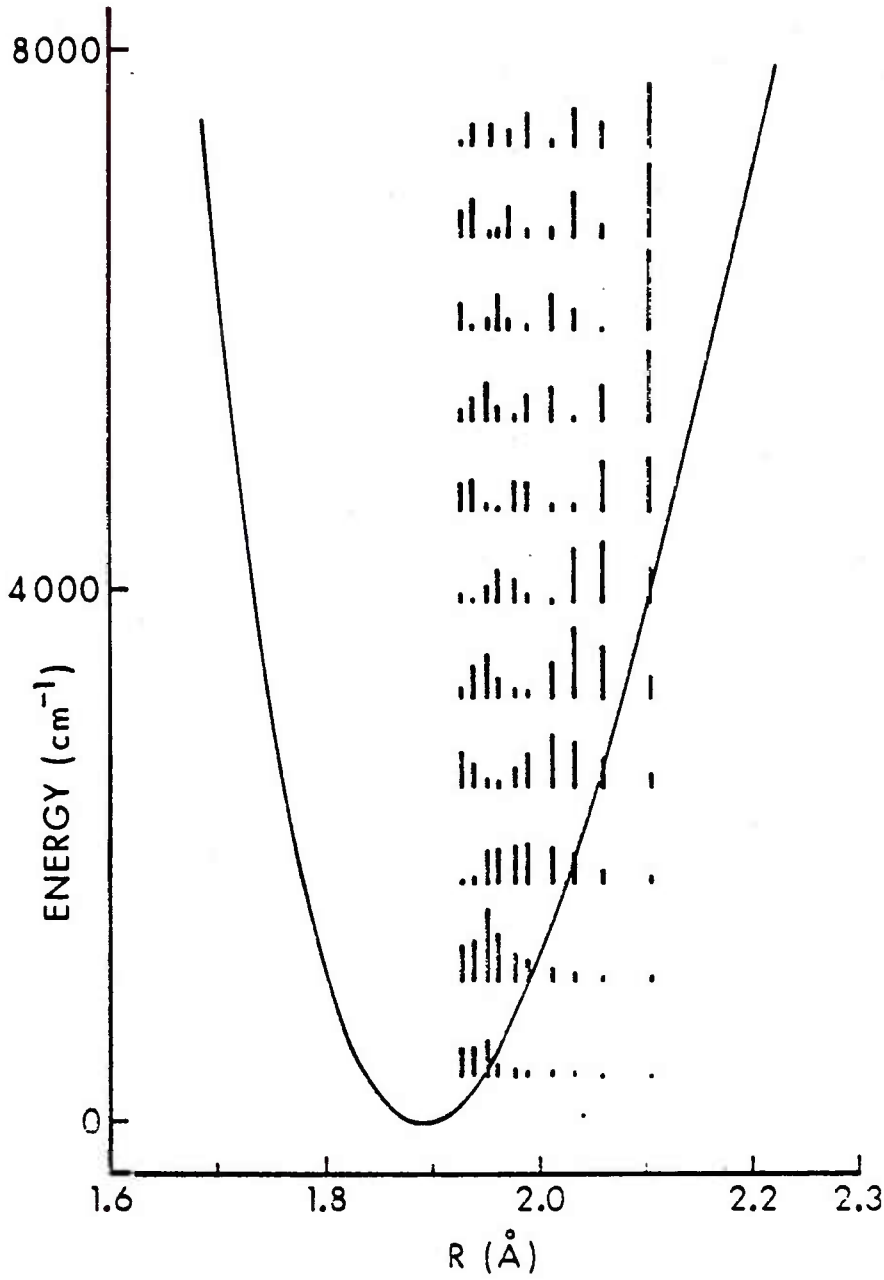

Figure 7. A plot of $q_{v'v''}$ vs. $r_L(v')$ as in Figure 6; see text. The curve is an independently plotted X-state RKR potential.

estimated intensities* indicate that 91% of the absorption strength out of v'' = 0 is to levels having v' > 10, while we have found that the overlap with these levels is only 75% of the total. This may indicate that the transition moment R_e is, on the average, about twice as large for the transitions to the predissociated levels as for the transitions to the bound ones. However, the likely variation in $R_e(r)$, on a state-by-state basis at high v', renders this result useful only as a rough guide, and not as a quantitative characterization.

Taken from the graph, Figure 2, of reference 15.

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APPENDIX A

The laser excites the S_2 in the center of a T-shaped cell, so that the emitted radiation passes through a layer ($\sim$ 4 cm) of S_2 vapor before reaching the exit window. At higher pressures, some of the fluorescence for low v'' bands will be absorbed by this layer. This absorption coefficient for the i^{th} band is proportional to $q_i F_i p$, where F_i is the fraction of molecules in the i^{th} ground state vibrational level and p is the S_2 pressure. Consequently,

$$(I_i/I_j)_{window} = (I_i/I_j)_{center} \exp\left[-cp\,(q_i F_i - q_j F_j)\right] \quad .$$

The correction is made empirically, using measurements of the ratio of the intensity of each band of interest to the intensity of a band with high enough v'' that the level has negligible population. A plot of the logarithm of the ratio vs. p provides a straight line which is used to extrapolate the measured intensity to that which would be observed at zero pressure. Typical necessary corrections to the strongest bands are about 20 percent, with an estimated 20 percent error in the amount of correction. This uncertainty is included in the $\delta q_{v'v''}$ values where appropriate.

APPENDIX B

The analysis for the rotational quantum numbers of the excited level depends primarily on the splitting between the main R and P branches of the rotationally resolved fluorescence (See Fig. 4a). To a first approximation (that is, neglecting the triplet splitting), the separation $\Delta\tilde{\nu}_{RP} = 4B_{v''}(J' + 1/2)$. Using this value of J' and knowledge of the triplet component involved (see below), an improved value of J' is calculated taking into account the influence of the triplet splitting (see reference 1 of text).

The occurrence of rotational satellites is expected (see reference 12 of text) in fluorescence from F_1 or F_3 levels in v' = 2, 6, and 7. The observation of a satellite may then be used to assign the triplet component involved, and the separation of the satellite from the nearest main branch provides further data on the value of J'. The results are summarized in the table where the columns labeled N' (main) and N' (satellite) list the quantum numbers obtained from the analysis of these respective splittings. Since only alternate rotational levels exist in the $B^3\Sigma_u^-$ state, the closest even value is used for the assignment.

There exists no prior information concerning the expectation of satellites (see reference 12 of text) in emission from v' = 8 or 9. None is observed here. In the case of v' = 9, a value of N' = 36 was obtained from the R-P splitting. The excitation was by an R-branch in the (9,0) band, measured to be at 35251 cm^{-1}. We compare this with a rotational analysis* yielding the values 32250, 35237, and 35241 cm^{-1} for $R_1(36)$, $R_2(36)$, and $R_3(36)$ respectively, to assign this excitation to the $F_1(36)$ level. Thus, v' = 9 does not have satellites and thus probably has a positive value of the triplet splitting parameter (see reference 12 of text). We do note that $F_1(36)$ is the highest bound level* in v' = 9 before the onset of predissociation. This could affect the presence or absence of satellite emission.

For v' = 8, we have no previous analysis which would yield a choice of triplet component. The excitation was R(28) in the (8,0) band, at 34858 cm^{-1}.

J. M. Ricks and R. F. Barrow, "The Dissociation of Gaseous Diatomic Sulfur", Can J. Phys., 47, 2423-2427 (1969).

SUMMARY OF RESULTS OF ROTATIONAL ANALYSIS

v'	N' (main)	Observed Satellite	N' (Satellite)	Assignment
2	46.0	$T_{R_{31}}$	43.9	$F_3(46)$
6	33.8	$N_{P_{13}}$	33.6	$F_1(34)$
7	30.4	$T_{R_{31}}$	27.5	$F_3(30)$
8	27.9	----	----	N'=28
9	35.7	----	----	$F_1(36)$

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